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"True" Hydrophilic-Lipophilic Balance of Polyoxyethylene Fatty Acid Esters Nonionic Surfactants

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GRAPHICAL ABSTRACT

This article proposes a set of equations that allow the calculation of the hydrophilic-lipophilic balance (HLB) value of polyoxyethylene esters from quality control data of the raw materials (fatty acids and polyethylene glycol) and the finished product (surfactant). The quality control data required include the acid value of the fatty acid, the hydroxyl value of the polyethylene glycol, and the hydroxyl value of the surfactant. Moreover, these calculations allow the determination of the mean relative molecular masses of the fatty acids, polyethylene glycol, monoesters, and diesters, and to calculate the proportion of polyoxyethylene monoester and polyoxyethylene diester. Models such as this would be of great utility for the rational design of emulsified products.

Keywords HLB, polyoxyethylene esters, quality control data, surfactants

1. INTRODUCTION

One of the critical requirements for the rational design of emulsions with optimal stability is the use the adequate emulsifier with the proper value of hydrophilic-lipophilic balance (HLB). Nonionic surfactants such as polyoxyethylene fatty acid esters (Figure 1) are widely used in pharmaceutical and cosmetical formulations as emulsifiers, especially the stearates.[1] In order to calculate the HLB of polyoxyethylene glycol esters, it is broadly used the method proposed by Griffin[2] in which the HLB value is equivalent to the mass (or weight) percentage of oxyethylene content divided by 5.[3] Another equation proposed by Griffin[2] that uses quality control data is Equation (1), which is strictly valid only for pure polyoxyethylene monoesters.[3]

$$HLB = 20\left(1 - \frac{S}{A}\right), \quad [1]$$

where S is the saponification number of the surfactant and A the acid number of the fatty acid. However, this form of calculation of the HLB value does not take into account the real composition of the ester, since the polyoxyethylene fatty acid esters nonionic surfactants are not substances chemically pure, but rather mixtures of monoesters, diesters, free polyoxyethylene glycol and free fatty acids.[4,5] Recently, Pasquali et al.[6] proposed a set of equations that

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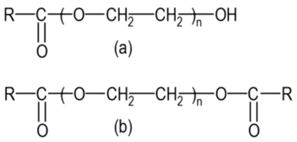

FIG. 1. (a) Polyoxyethylene fatty acid monoester and (b) polyoxyethylene fatty acid diester.

allows the calculation of the HLB value of polyoxyethylene esters from quality control data of the raw materials and the finished product. These data include the acid value of the fatty acid, the hydroxyl value of the polyethylene glycol, and the hydroxyl value of the surfactant. However, the application of those equations is restricted to polyoxyethylene glycol free polyoxyethylene esters obtained by esterification.

In order to solve those limitations, in this article we propose a set of equations that allow the calculation of the true HLB value for a certain production batch from polyoxyethylene esters using quality control data of the raw materials (fatty acids and polyethylene glycol) and the finished product (surfactant) taking into account the true composition of the surfactant of both, the obtained by esterification as well as the obtained by reaction of fatty acid with ethylene oxide.

2. METHODS

Polyoxyethylene esters can be obtained by esterification and by formation of adducts of ethylene oxide[7,8] (Figures 2 and 3).

2.1. Polyoxyethylene Esters Obtained by Esterification

The data required to calculate the HLB value of the polyoxyethylene esters obtained by esterification are these:

a) saponification value of the surfactant (S);
b) hydroxyl value of the surfactant ($N_{OH\ surf}$);
c) hydroxyl value of the polyoxyethylene glycol ($N_{OH\ PEG}$);
d) acid value of the fatty acid (A_{acid});
e) acid value of the surfactant (A_{surf});
f) mass fraction of free polyoxyethylene glycol ($f_{free\ PEG}$).

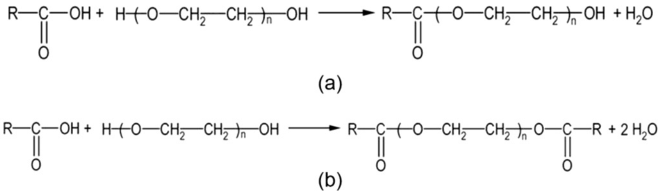

FIG. 2. Reactions to obtain (a) polyoxyethylene fatty acid monoesters and (b) polyoxyethylene fatty acid diesters by esterification of fatty acids with polyoxyethylene glycol.

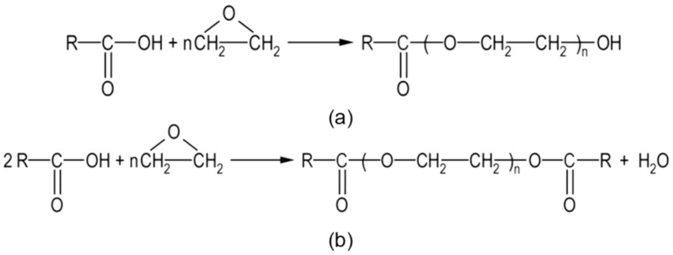

FIG. 3. Reactions to obtain (a) polyoxyethylene fatty acid monoesters and (b) polyoxyethylene fatty acid diesters by formation of adducts of ethylene oxide.

The sequence of the calculations is as follows:

1) relative molecular mass of fatty acid [$Mr(acid)$];
2) relative molecular mass of polyoxyethylene glycol [$Mr(PEG)$];
3) relative molecular mass of monoester [$Mr(monoester)$];
4) relative molecular mass of diester [$Mr(diester)$];
5) mean ethylene oxide units per molecule of surfactant (n_{EO});
6) mean fraction of free fatty acid ($f_{free\ acid}$);
7) amount of free fatty acid in mol/g of surfactant ($n_{free\ acid}$);
8) amount of free polyoxyethylene glycol in mol/g of surfactant ($n_{free\ PEG}$);
9) amount of monoester in mol/g of surfactant ($n_{monoester}$);
10) amount of diester in mol/g of surfactant ($n_{diester}$);
11) mass fraction of diester ($f_{diester}$);
12) mass fraction of monoester ($f_{monoester}$);
13) HLB of the monoester ($HLB_{monoester}$);
14) HLB of the diester ($HLB_{diester}$);
15) HLB of the surfactant ($HLB_{surfactant}$).

To obtain values of these 15 unknowns, are solved the following 15 equations:

$$Mr(acid) = \frac{1000 \times Mr(KOH)}{A_{acid}}, \qquad [2]$$

where $Mr(KOH)$ is the relative molecular mass of potassium hydroxide.

$$Mr(PEG) = \frac{2 \times 1000 \times Mr(KOH)}{N_{OH_{PEG}}} \qquad [3]$$

$$Mr(monoester) = Mr(PEG) + Mr(acid) - Mr(H_2O) \qquad [4]$$

$$Mr(diester) = Mr(monoester) + Mr(acid) - Mr(H_2O) \qquad [5]$$

$$n_{EO} = \frac{Mr(PEG) - Mr(H_2O)}{Mr(EO)} \qquad [6]$$

$$f_{free\,acid} = \frac{Mr(acid) \times A_{surf}}{1000 \times Mr(KOH)} \qquad [7]$$

$$n_{free\,acid} = \frac{f_{free\,acid}}{M(acid)}, \qquad [8]$$

where $M(acid)$ is the molar mass of the fatty acid [$M(acid)$ is numerically equal to $Mr(acid)$].

$$n_{free\,PEG} = \frac{f_{free\,PEG}}{M(PEG)}. \qquad [9]$$

In determining the hydroxyl value of the surfactant, per mole of free polyoxyethylene glycol, the equivalent of 2 mole of potassium hydroxide is consumed. While for each monoester mole, the equivalent of 1 mole of potassium hydroxide is consumed. In consequence, the hydroxyl value of the surfactant is equal to:

$$N_{OH_{surf}} = \left(2n_{free\,PEG} + n_{monoester}\right) \times 1000 \times M(KOH)$$

Therefore, the amount of monoester in mol/g of surfactant is:

$$n_{monoester} = \frac{N_{OH_{surf}}}{1000 \times M(KOH)} - 2n_{free\,PEG} \qquad [10]$$

On the other hand, in determining the saponification value, for each mole of monoester or free fatty acid, it is consumed the equivalent of 1 mole of potassium hydroxide; and for each mole of diester, the equivalent of 2 mol of potassium hydroxide is consumed.

$$S = (n_{monoester} + 2n_{diester} + n_{free\,acid}) \times 1000 \times M(KOH)$$

Therefore, the amount of monoester in mol/g of surfactant can also be calculated with the following equation:

$$n_{monoester} = \frac{S}{1000 \times M(KOH)} - n_{free\,acid} - 2n_{diester} \qquad [11]$$

Equating (10) and (11) to calculate the amount of monoester in mol/g of surfactant we obtain:

$$\frac{S}{1000 \times M(KOH)} - n_{free\,acid} - 2n_{diester} = \frac{N_{OH_{surf}}}{1000 \times M(KOH)} - 2n_{free\,PEG}$$

Therefore, the amount and mass fraction of diester in mol/g of surfactant and the mass fraction of monoester are:

$$n_{diester} = \frac{S - N_{OH_{surf}}}{2 \times 1000 \times M(KOH)} - \frac{n_{free\,acid}}{2} + n_{free\,PEG} \qquad [12]$$

$$f_{diester} = n_{diester} \times M(diester) \qquad [13]$$

$$f_{monoester} = n_{monoester} \times M(monoester) \qquad [14]$$

Finally, the three equations below allow the calculation of the HLB values of the monoester, the diester and the surfactant:

$$HLB_{monoester} = 20 \times \left(1 - \frac{Mr(acid)}{Mr(monoester)}\right) \qquad [15]$$

$$HLB_{diester} = 20 \times \left(\frac{Mr(diester) + Mr(H_2O) - 2Mr(acid)}{Mr(diester)}\right) \qquad [16]$$

$$HLB_{surf} = \frac{f_{monoester} \times HLB_{monoester} + f_{diester} \times HLB_{diester}}{f_{monoester} + f_{diester}} \qquad [17]$$

2.2. Polyoxyethylene Esters Obtained by Formation of Adducts of Ethylene Oxide

The data required to calculate the HLB of polyoxyethylene esters obtained by formation of adducts of ethylene oxide are:

a) saponification value of the surfactant;
b) hydroxyl value of the surfactant;
c) mean ethylene oxide units per molecule of surfactant;
d) acid value of the fatty acid;
e) acid value of the surfactant;
f) mass fraction of free polyoxyethylene glycol.

The sequence of calculations is as follows:

1) relative molecular mass of fatty acid;
2) relative molecular mass of polyoxyethylene glycol;
3) relative molecular mass of monoester;
4) relative molecular mass of diester;
5) amount of free polyoxyethylene glycol in mol/g of surfactant;
6) amount of monoester in mol/g of surfactant;
7) mass fraction of monoester;
8) mass fraction of free fatty acid;
9) amount of free fatty acid in mol/g of surfactant;
10) amount of diester in mol/g of surfactant;
11) mass fraction of diester;
12) HLB of monoester;
13) HLB of diester.
14) HLB of surfactant.

To obtain the values of these 14 unknowns, the following 14 equations are solved. The relative molecular mass of fatty acid is obtained with Equation (2) and the relative molecular mass of free polyoxyethylene glycol is calculated with Equation (18).

$$Mr(PEG) = n_{EO} \times Mr(EO) + Mr(H_2O) \qquad [18]$$

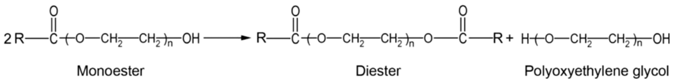

FIG. 4. Decomposition reaction of a polyoxyethylene fatty acid monoester.

The relative molecular masses of the monoester and the diester are calculated, with Equations (19) and (5), respectively:

$$Mr(monoester) = Mr(acid) + n_{EO} \times Mr(EO) \qquad [19]$$

To obtain the amount of free polyoxyethylene glycol in mol/g of surfactant is used Equation (9). This fraction originates from the breakdown of the monoester [4] (Figure 4).

The amount of monoester in mol/g of surfactant and the mass fraction of monoester are calculated with Equations (10) and (14), respectively; while the mass fraction of free fatty acid is obtained with Equation (7) and the amount of free fatty acid in mol/g of surfactant with Equation (8). The amount of diester in mol/g of surfactant is calculated with Equation (12) and the amount of monoester with Equation (10). Finally, the HLB values of the monoester, the diester and the surfactant are calculated with Equations (15), (16), and (17).

In both methods of obtaining polyoxyethylene esters should be checked at the end that the sums of the mass fractions of the monoester, diester, free polyoxyethylene glycol and free fatty acid are equal to 1 or to a value close to 1. A value for this sum very different from 1 indicates that some data is incorrect.

3. RESULTS AND DISCUSSION

In Tables 1 and 2, we show the results of applying the equations proposed in this paper to the polyoxyethylene esters obtained by esterification and by formation of adducts of ethylene oxide, respectively.

Tables 1 and 2 show that:

1) raising the hydroxyl value of the polyoxyethylene glycol used in the method of production of surfactant by esterification decreases the HLB value, as it decreases its relative molecular mass;
2) raising the acid value of the fatty acid increases the HLB value because it decreases the ratio of the relative molecular mass of the fatty acid and of the monoester (Equation (14));
3) an increase in acid value of the surfactant causes a decrease in the HLB value;

TABLE 1

Examples of calculations of HLB value of polyoxyethylene esters obtained by esterification

Data					
S	82	82	82	82	82
$N_{OH\ surf}$	93	93	93	93	93
$N_{OH\ PEG}$	280	290	280	280	280
A_{acid}	200	200	210	200	200
A_{surf}	0	0	0	2	0
$f_{free\ PEG}$	0.1000	0.1000	0.1000	0.1000	0.2000
Unknowns					
$Mr(acid)$	280.53	280.53	267.17	280.53	280.53
$Mr(PEG)$	400.76	386.94	400.76	400.76	400.76
$Mr(monoester)$	663.27	649.45	649.91	663.27	663.27
$Mr(diester)$	925.79	911.97	899.07	925.79	925.79
nOE	8.69	8.38	8.69	8.69	8.69
$f_{free\ acid}$	0.000	0.000	0.000	0.010	0.000
$n_{free\ acid}$	0.000000	0.000000	0.000000	0.000036	0.000000
$n_{free\ PEG}$	0.000250	0.000258	0.000250	0.000250	0.000499
$n_{diester}$	0.000151	0.000160	0.000151	0.000134	0.000401
$f_{diester}$	0.1403	0.1463	0.1362	0.1238	0.3713
$n_{monoester}$	0.0012	0.0011	0.0012	0.0012	0.0007
$f_{monoester}$	0.7684	0.7408	0.7529	0.7684	0.4374
$HLB\ monoester$	11.5	11.4	11.8	11.5	11.5
$HLB\ diester$	8.3	8.1	8.5	8.3	8.3
$HLB\ surfactant$	10.1	9.8	10.2	10.0	8.8
Sum of fractions	1.0087	0.9871	0.9891	1.0022	1.0087

TABLE 2
Examples of calculations of HLB value of polyoxyethylene esters obtained by formation of adducts of ethylene oxide

Data					
S (mg of KOH/g)	87	87	87	87	87
$N_{OH\ surf}$ (mg of KOH/g)	93	93	93	93	93
n_{EO}	8	8.2	8	8	8
A_{acid} (mg of KOH/g)	200	200	201	200	200
A_{surf} (mg of KOH/g)	0	0	0	1	0
$f_{free\ PEG}$	0.1000	0.1000	0.1000	0.1000	0.2000
Unknowns					
$Mr(acid)$	280.53	280.53	279.13	280.53	280.53
$Mr(free\ PEG)$	370.42	379.23	370.42	370.42	370.42
$Mr(monoester)$	632.93	641.74	631.53	632.93	632.93
$Mr(diester)$	895.45	904.26	892.65	895.45	895.45
$n_{free\ PEG}$ (mol/g)	0.000270	0.000264	0.000270	0.000270	0.000540
$n_{monoester}$ (mol/g)	0.001118	0.001130	0.001118	0.001118	0.000578
$f_{monoester}$	0.7074	0.7253	0.7058	0.7074	0.3656
$f_{free\ acid}$	0.0000	0.0000	0.0000	0.0050	0.0000
$n_{free\ acid}$ (mol/g)	0.000000	0.000000	0.000000	0.000018	0.000000
$n_{diester}$ (mol/g)	0.000216	0.000210	0.000216	0.000208	0.000486
$f_{diester}$	0.1939	0.1901	0.1933	0.1859	0.4356
$HLB_{monoester}$	11.1	11.3	11.2	11.1	11.1
$HLB_{diester}$	7.9	8.0	7.9	7.9	7.9
HLB_{surf}	10.4	10.6	10.5	10.5	9.4
Sum of fractions	1.0013	1.0154	0.9991	0.9983	1.0013

4) an increase of the free polyoxyethylene glycol fraction leads to a decrease in the HLB value since the formation of polyoxyethylene glycol also produced diester;
5) raising the mean ethylene oxide units per molecule of surfactant increases the HLB value.

4. CONCLUSIONS

To calculate the HLB value of the esters of polyethylene glycols, Griffin proceeded under the assumption that the actual composition of bulk chemicals coincides with the theoretical composition, i.e., that the fatty acid composition is 100% pure, that the amount of ethylene oxide units is exactly equal to the declared, that there is no free fatty acid or polyethylene glycol, that in the case of monoesters the proportion of diesters is zero, or that for the diesters the proportion of monoester is also zero. However, none of these assumptions is correct for standard chemicals; therefore the HLB values obtained by Griffin for these nonionic surfactants are rather an approximation to the true values.

The proposed equations allow the calculation of the real HLB values of polyoxyethylene esters from quality control data of the fatty acids, polyoxyethylene glycols and surfactants, both obtained by esterification and by formation of adducts of ethylene oxide. In addition, these equations also allow us to know the average relative molecular masses of the polyethylene glycol fatty acid used as raw materials, the monoester and diester formed. Moreover, we can also calculate the proportions of these last two, as well as the fatty acid that may have been in the final product unreacted and the average number of ethylene oxide units per molecule of surfactant. All this information could be added by the manufacturer on the certificate of analysis of the surfactant using only the results of the tests that are commonly used in quality control and would contribute to the better design of emulsions with improved stability.

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